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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

GEOLOGICAL SURVEY OF CANADA
TOPICAL REPORT NO. 85

VISITS TO EUROPEAN AND BRITISH LABORATORIES ENGAGED IN ISOTOPIC STUDIES AS APPLIED TO GEOLOGICAL PROBLEMS

BY
R. K. WANLESS

OTTAWA
1964

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INTRODUCTION

This report presents information obtained in the course of visits to European and British laboratories engaged in isotopic studies as applied to geological problems. The original itinerary covered visits to twenty-one institutions in Holland, Belgium, France, Italy, Switzerland, Germany and England. In addition, it proved possible to contact scientists in Zurich and Hanover. The laboratories visited, and the scientists contacted, are listed in chronological order in Appendix I.

Preliminary plans were made to include visits to laboratories in Denmark, Sweden and Finland, but due to the dictates of time and the complicated pecularities of airline round-trip fare structures, it was not deemed practical to include the Scandanavian visits in this trip.

The laboratory visits were all made between April 22nd and May 25th, 1963. This period proved to be most convenient, both from the point of view of the scientists contacted, and the weather encountered. Since the spring terms in the various institutions had not finished, no problems were encountered in making arrangements to visit the laboratories. The weather was excellent and no cancellations of airline flights were experienced.

All details re travel and accommodations in Europe were handled through a local travel agency. This arrangement proved to be quite satisfactory and no serious complaints can be registered with regard to the hotels selected. A list of hotels is included in Appendix 2.

Since rail travel in Europe is generally more convenient than air travel, a Eurail Pass was purchased and found to be most advantageous.

This pass, which must be obtained before leaving North America, provides for unlimited first-class rail travel in any of 13 European countries (excluding Britain) during a specified period. Since it is not necessary to purchase individual trip tickets a great deal of time is saved and, in addition, the system permits the maximum in itinerary flexibility.

OBJECTIVES

The trip provided an opportunity to:

(1) make personal contact with scientists actively engaged in the fields of stable isotope studies and isotopic age determinations in Europe,

(2) observe the experimental methods being employed, and under development,

(3) discuss research projects being undertaken, and the relative merits of the techniques being employed to solve the problems,

(4) familiarize myself with the various types of specialized equipment used in the laboratories and available on the European market, and

(5) when possible, to study the organizational arrangement of the various institutions with respect to the functioning of the isotope laboratories.

LABORATORIES VISITED

1. Holland

The Laboratory for Isotope Geology - Amsterdam

The Laboratory for Isotope Geology, under the direction of Dr. H.N.A. Priem, is currently occupying space in the Laboratory for Mass Separation, at 407 Kruislaan and at the University of Amsterdam, Nieuwe Prinsengracht 130. New buildings are now under construction in another section of the City and Dr. Priem expects to move all equipment to a single location during 1964.

The group, consisting essentially of Dr. Priem and Dr. N.A.I.M. Boelrijk (Chemist) assisted by three technicians, has functioned in borrowed space at both of the above listed institutions. While this has certainly had its disadvantages generally, they have benefited greatly through the professional and technical assistance provided by the staff of the Laboratory for Mass Separation under the direction of Dr. J. Kistemaker. Specifically, Dr. A.J.H. Boerboom (Physicist) and Dr. T. van der Hauw (electrical engineer) have designed and assembled the mass spectrometer and associated electronic equipment used by the isotope group, and they have contributed significantly to the success of the endeavour through their continued interest in the operational aspects of the equipment. All of the electrical components were assembled in the laboratories of the Laboratories for Mass Separation and all instrumental parts were fabricated in the laboratory instrument shop.

The mass spectrometer, is a very large (12" radius of curvature) instrument, embodying many automatic features in both the electronic and vacuum aspects. Many of these are by no means essential to its satisfactory operation, and in fact, may often contribute to the accumulated 'down time' through failure of ancillary components. Of particular interest to the author, was a vacuum lock arrangement designed to permit the rapid introduction of solid samples without the loss of high vacuum. (Pictures of this apparatus are on file in the Isotope and Nuclear Geology Section). This is an especially advantageous arrangement since the instrument has been designed primarily for the analysis of solids. A very simple solid source filament assembly is used in conjunction with the vacuum lock. The filaments are mounted on the pins of a normal minature octal tube base obtained in quantity from Philips Electronic Ltd. The tube base, with its associated filaments, is simply plugged into the appropriate receptacle in the vacuum lock and is precisely positioned with respect to the source plates when the mechanism is moved to the operating position. The filament support assemblies are so cheap that they may be discarded after each analysis thereby reducing the problems of possible cross contamination between subsequent samples.

Rb/Sr Age Determinations

Dr. Priem's group is currently calibrating the isotope dilution solutions required for rubidium and strontium determinations necessary for Rb/Sr age measurements. At the time of the writer's visit no age measurements has been carried out using this method. It has been our pleasure to supply Dr. Boelrijk with a small quantity of 'Spec.' pure RbCl to assist him in his calibration work. The chemical procedures employed are essentially those published by H.L. Allsopp (Journal of Geophysical Research <u>66</u>, 1499-1508 (1961) with the exception of the fact that Rb samples were placed on the mass spectrometer filament as the perchlorates rather than converting them to the sulphate form. Strontium samples are placed on the filament as chlorides. Every effort is made to keep the quantity of reagents as small as possible in order to reduce the introduction of contaminants and extensive use is made of small lucite boxes in which samples are stored during various stages of the preparation. The procedures are designed to use 200 mgm samples of mica per determination. This quantity of sample will be ample material for analysis with the mass spectrometer which has sufficient sensitivity to detect a 1 μgm sample of Rb or Sr.

K-Ar age Determinations

Plans are also being made to assemble the equipment required for potassium-argon age determinations. The apparatus now on hand will be tested, but will not be put into operation until the move to permanent quarters is complete. The installation includes a 6KW Philips hi-frequency generator (identical to the unit in the G.S.C. Laboratories) to be used for the vacuum fusion of the micaceous mineral concentrates. A novel system of argon-38 spike measurement is to be incorporated. This is to comprise a precisely knownsmall volume which is to be attached to a large volume containing the enriched isotope stock. Spring loaded end pieces are to be used to seal the calibrated volume and to permit the passage of the gas from the large resevoir and to the sample chamber. The volumes are to be of such dimensions that approximately 1000 spike aliquots may be removed from the large resevoir without appreciably lowering the gas pressure in the resevoir. While one may experience some difficulties with the initial determination of the pressure in the resevoir the system should result in a considerable saving in time over the method currently employed in our laboratories.

A second mass spectrometer is being assembled for the argon work. In this instance the analyzer tube (a glass Reynolds type) and magnet assembly have been purchased from Nuclide Analysis Associates, State College, Pennsylvania, while the electronic components are to be purchased from Atlaswerke in Bremen, Germany. The American made components have been forwarded to the German plant where the final assembly of the electronics and initial testing will be carried out.

In another section of the Laboratory for Mass Separation I was shown a model CH4 Atlaswerke mass spectrometer. This instrument is very popular in European laboratories and I subsequently saw several different models during the later stages of the trip. The CH4 mass spectrometer has a 6" radius analyzer tube and may be used for either gaseous or solid analyses. When used for solid analyses a vacuum lock arrangement is provided for rapid change of samples. In addition, the instrument is equipped with heating units which permit extensive baking of all portions of the vacuum system, or alternatively, the baking of the source areas only. The mass spectrometer suffers somewhat in my opinion from the multitude of automatic controls incorporated to permit its application in a variety of fields. However, these accutrements appear to be very well designed and consequently do not contribute significantly to maintenance problems.

Zircon Age Determinations

Plans for future studies by the group are to include work on materials from Portugal, Spain and from the Brazilian Shield in Dutch Guiana. In addition to the proposed age determinations based on Rb/Sr and K/Ar measurements, work is to be carried out on zircon concentrates and mineral separation equipment has been acquired and set up in the laboratories at the University of Amsterdam. It is intended that detailed zircon studies be carried out with age measurements being determined for the various grain sizes of zircon. To achieve the mineral separations a series of 5 or 6 glass columns some 6 feet long and varying in diameter from approximately $1\frac{1}{2}$" to 3" have been set up in series so that the flow from the top of one column is fed to the bottom of the next larger column etc. The water flow is decreased as the diameter increases and the lighter fractions are carried progressively further through the system. The output of the final column (finest fraction) is then placed on a very large Wilfley type table(made in Germany by Wedag. Pictures are on file in the Isotope and Nuclear Geology Section), where final purification is performed. The Wedag table has a special composition top into which have been machined a series of parallel grooves. Dr. Priem was most enthusiastic about the design of the table and remarked on the ease with which the table top could be cleaned between operations. Most tables of this nature have strips of wood nailed on the top to form the grooves and are consequently much harder to clean after use.

Several zircon concentrates have been processed in anticipation of the age measurements to be carried out. Dr. Priem reports that he finds the greatest radioactivity concentrated in the smallest size fraction. The results from all fractions will be compared on a "Concordia" plot in order to determine the most probable age of the material and to demonstrate the effect of losses or additions of parent or daughter products subsequent to the final crystallization of the zircon.

Dr. Priem has also designed and assembled a small apparatus to carry out mineral separations based on the dielectric properties of minerals, specifically the separation of xenotime from zircon concentrates.

The sample is placed in a plastic hopper in a liquid having the proper density and a pair of electrodes, (with a gap of approximately 2 mm.) having roughly 1000V D.C. applied across them, are slowly drawn through the solution containing the sample. The mineral grains are held between the electrodes while under the surface of the liquid but are dropped when drawn out of solution. The electrodes are mechanically returned to the solution and the operation is repeated. The desired mineral is thus slowly concentrated beyond the end of the plastic hopper. (Pictures are on file in the Isotope and Nuclear Geology Section).

Carbon-14 Enrichment

While at the Laboratory for Mass Separation it was my pleasure to talk with Dr. A.E. De Vries who has set up and operated a gaseous thermal diffusion apparatus to enrich the C^{14} concentration of samples of CO for radiocarbon age measurements. The work has been carried out for the radiocarbon dating laboratory in Gronigen, The Netherlands. In order to extend the range (to 70,000 or 80,000 years) of natural radiocarbon age measurements the concentration of the radioactive C-14 molecule must be increased. Dr. De Vries has used a thermal diffusion apparatus comprising 9 columns in parallel to accomplish an enrichment of from 8 to 10 times the original C-14 activity. A limitation on the process is encountered in the necessity for very large samples of carbonaceous material required to provide approximately 200 litres of CO. The desired enrichment is attained after the columns have been in operation for a period of from four to six weeks and the extent of the enrichment process is determined by monitoring the change in the O^{18} concentration mass spectrometrically. (A picture of the apparatus is on file in the Isotope and Nuclear Geology Section).

2. Belgium

The Institut de Physique, Université Libre de Bruxelles

This group, under the direction of Professor E. Picciotto, is presently located in a series of basement laboratories which are somewhat crowded and old-fashioned. However, a new physics building is well advanced and modern laboratories are to be made available for their work.

Professor Picciotto has worked very closely with Dr. Cahen on problems originating in the Belgian Congo. These studies have embodied both Rb/Sr and Pb/U, Pb/Th age measurements and it would appear that this aspect of the work will continue with the addition of K/Ar measurements to help complete the picture. Studies of other North African materials, primarily from Algeria have also been carried out. Some problems have been encountered in the latter region in that Rb/Sr, K/Ar and zircon age determinations for the crystalline basement yield, for the most part, dates of 500 m.y., but this region is overlain by Precambrian formations. In addition to the age determinations referred to above Dr. Picciotto is currently devoting much of his time to studies of the oxygen and hydrogen isotope ratios in core samples of snow from Antarctica.

Chemical Techniques

Dr. S. Deutsch is primarily concerned with the chemical preparation of sample materials for mass spectrometric analyses. The procedures employed are essentially the same as those published by Dr. E. Jäger for Rb/Sr and by Dr. G. Tilton for zircons. Of particular interest was a special fume hood used for perchloric acid work. The hoods are fabricated in Belgium of transparent poly-vinyl chloride (PVC- trade name COVIDUR). The inner corners are all well rounded to permit easy cleaning and to prevent the accumulation of undesirable compounds. The structural frame for the sliding door is made of opaque PVC thus eliminating the necessity for any wooden components. Dr. Deutsch has found the hoods to be resistant to perchloric acid fumes and reports that they are ideally suited to this type of work. Enquiries re a Canadian supplier for an equivalent unit are now underway.

Extensive use is also made of home-designed lucite boxes to help keep the contamination levels as low as possible. These boxes, roughly 2' x 2' x 2' are fitted with a counter balanced, sliding fronts to facilitate easy access. All ion exchange columns (approximately 12" long by ½" diameter) are kept in the boxes and other time consuming steps in the chemical procedures are also carried out in the protected areas. In addition nitrogen gas is permitted to flow over the teflon beakers used for evapourations in a manner similar to the procedures used in Patterson's laboratory at the California Institute of Technology in Pascadena, California.

The zircon age measurements, mainly of Hercynian materials, are at present not being carried out on different families or size fractions. Samples ranging from 5-50 kilograms are crushed and the zircons separated. A pure zircon concentrate containing all zircons is then used for the age determination. It would appear that this procedure may be somewhat risky, as it could certainly contribute to uncertainty when attempts are made to interpret the observed age distribution which may be a reflection of zircons with more than one proveniance combined in unknown proportions. Dr. Picciotto has extracted a quantity of Th^{230} from a Katanga pitchblende for use as a spike when determining the thorium concentration in zircons by means of isotope dilution techniques.

Mass Spectrometry

Dr. R. Delwiche is responsible for the construction and operation of the mass spectrometric equipment. At present one mass spectrometer is in operation and a second Reynolds type glass analyzer tube (built in Bern) is being assembled for argon analyses. The unit being used for the Rb, Sr, Pb, U and Th analyses is a very large instrument embodying a 60° analyser tube, a 14 stage electron multiplier built in Zurich, and an enormous vacuum lock to facilitate the introduction of samples without loss of the primary vacuum (approximately 20 minutes are required to change samples). I was informed that the original design work was carried out by Dr. J. Geiss of the University of Bern and that most of the assembly was completed in Brussels. The instrument embodies many automatic control appendages, as does the mass spectrometer in Amsterdam and one cannot help but wonder how much actual time is lost servicing the ancillary items that are far from essential to the satisfactory operation of the instrument. Most vacuum ports etc. have also been assembled on a gigantic scale and there are a multitude of vacuum joints which I would judge must contribute to problems of initial vacuum and of outgassing of the large surface areas. The latter problem may explain in part the incorporation of very large vacuum pumps (100 litre/sec, Leybold Hg pumps) and special ballast volume between the diffusion and fore pumps.

Very long (2") tantalum filaments (Dr. Delwiche finds both W and Re filaments contain hydrocarbon impurities) are used for both the centre and side filaments. The sample fialment has a transverse kink formed in it at the midpoint and the sample material is deposited in this depression. One extremely interesting comment concerned the analysis of strontium in the presence of traces of rubidium remaining after the ion exchange treatment. Dr. Delwiche has found that by 'flashing' the filament at 5 Amps for 1 second the majority of the interfering Rb may be expelled. He reports that it is now possible to carry out a Sr analysis in two hours using this method, as opposed to the older technique whereby the filament was left at a low temperature overnight in order to reduce the Rb contamination to a negligible level.

Rubidium and strontium samples in the 5 μgm range are routinely handled and it has been noted that the isotope fractionation during the run amounts to approximately 2% for strontium samples. A double spiking technique employing enriched Sr^{84} and Sr^{86} samples is used in order to establish the correction required.

Lead samples are placed on the filament with boric acid and are commonly handled in the 5 μgm range. Before my visit I had been advised that this group had developed techniques for the analysis of lead samples in the 1 μgm range using an ammonium nitrate flux on the filament. This information was apparently erroneous and I was advised that the technique had not been tried at Brussels.

Some analyses of magnesium samples have been carried out. For this work the instrument was equipped with two filaments (both tantalum) and the sample was placed on one filament as a mixture of MgO + BeO + oxalic acid. When Mg^+ ions begin to appear freon gas (dichlorodifluoromethane CCl_2) or fugene 12 is admitted to the instrument and the pressure is permitted to increase from 10^{-7} to 10^{-5} mm of Hg. Under these conditions the Mg^+ ion currents are enhanced by a factor of 10 and satisfactory analyses may be carried out. Dr. Delwiche could not give me any idea regarding the magnitude of variations between replicate analyses of the same material and I was left with the distinct feeling that while it had been possible to produce satisfactory ion currents in this manner no serious work had been undertaken. However Dr. Delwiche advised me that it was possible to carry out analyses on samples containing 10 μgms of magnesium and that he felt the method might be improved upon to the stage where 1 μgm samples would be sufficient.

K-Ar Age Determinations

Equipment is now being assembled for K-Ar age determination studies. A Reynolds type glass, 60° analyser tube is being set up and, in addition, the induction heating equipment and high vacuum extraction lines required for argon extraction and purification are being built.

Radiocarbon Dating Laboratory, University of Louvain

A very brief visit was paid to the C-14 dating laboratory at the University of Louvain in the Parc D'Arenberg at Hévérle some 25 miles from Brussels. This laboratory group was in the early stages of a move to new space in a recently completed science building, consequently none of the apparatus was operating. However, Dr. E. Crèvecoeur very kindly described the equipment to me and took me on a short tour of the new laboratories.

The C-14 counting equipment is being assembled in a well in the ground floor of the new building. When the installation is complete, layers of iron are to be placed over the unit and a temporary floor installed. Laboratory traffic will then be able to pass freely over the area which is located in the sample preparation room. While a considerable space saving is realized with this arrangement it would appear that problems re contamination, and difficulties in servicing, would far outweigh the space advantages. Of course some additional shielding will be provided by the adjacent concrete walls of the well.

All C-14 measurements are carried out as CH_4 after conversion from CO_2 by means of a nickel catalyst. The samples are counted at 3 atmospheres pressure in a copper counter with 19 anti-coincidence counters, operating in the proportional range, built around the outer circumference of the counter. The arrangement is not unlike the type designed by Oeschger at Bern. Dr. Crèvecoeur is very enthusiastic in his recommendation of the use of methane as a sample gas, pointing out that he obtains a very long plateau with little slope when the unit is operated at three atmospheres and that sample purification is easy.

In addition to his work with C-14 Dr. Crèvecoeur is experimenting with some very small copper proportional counters to be used for the measurement of the Al^{26} activity in meteorites.

Musee Royal De l'Afrique Centrale

The opportunity was taken to visit Dr. L. Cahen, the Director of the Royal Museum at Tervuren, some 10 miles from Brussels. No laboratory equipment is installed at the museum and all of the isotope work being carried on by Dr. Cahen is being handled by Dr. Picciotto's group at the Université Libre de Bruxelles.

Dr. Cahen's interest has centred on the age relationship in the Belgian Congo and he has published extensively on the subject. He is now an enthusiastic proponent of the isotopic age determination approach and is keen to use all methods of age measurement in order to unravel the various tectonic events of the region. He has recently published an outline of the structural regions of Central Africa embodying the most recent age results.

3. France

Centre D'Études Nucléaires De Saclay, Paris

The invitation to visit the French Atomic Energy establishment at Saclay, some 25 kilometers from Paris, was received from an old friend, Dr. Etienne Roth, who is in charge of the mass spectrometric laboratories. Unfortunately, a change of schedule after the original itinerary was finalized, made it impossible for him to be present during my visit but I was shown the laboratories by Drs. G. Dirian and Marc Dupuis.

At Saclay I presented a paper, illustrated with slides, of the isotope work being undertaken at the Geological Survey of Canada. The seminar was attended by about 50 scientists, and a lively question period followed. I believe they were pleased to learn of the activities of our laboratory.

The laboratories at Saclay are of course closely associated with studies in the nuclear field and consequently the mass spectrometric application differs considerably from our own. From time to time, however they have carried out lead, uranium and thorium analyses for groups in France in Belgium. In addition, many projects involving variations of H/D and oxygen in the water cycle, in materials from Antarctica, in air circulation, and in laboratory experiments have been undertaken.

Mass Spectrometric Apparatus

I was amazed at the concentration of mass spectrometric apparatus in one area, and I was told that there were other laboratory groups, more closely associated with pile control functions, where other mass spectrometers were installed. A total of 12 instruments are in use in the laboratories, including two A.E.I. (Associated Electronic Industries, formerly Metropolitan Vickers) M.S. 5 solid source mass spectrometers, 2, A.E.I. M.S. 2 units, several French instruments made by Thompson-Houston, and in addition an assortment of instruments assembled in the Saclay laboratories for special projects. One could not help but feel that they were prepared to build an instrument whenever one was required for a specific experiment. Several of the analyser tubes were made of copper and some of the units designed for low mass work were equipped with permanent magnets rather than electro magnets.

All of the mass spectrometers were equipped with D.C. amplifiers as were the instruments in Holland and Belgium. It is indeed surprising that the advantages to be realized from the incorporation of vibrating reed type amplifiers have been completely ignored by the majority of the European laboratories.

The very large M.S. 5 mass spectrometers, referred to above, are used extensively for the analysis of uranium and plutonium and are ideally suited to work in the high mass range. Both are equipped with vacuum locks to facilitate the rapid introduction of solid samples and both embody electron multiplier detection assemblies. The analysis of 1 μgm. samples of U and Pu may be handled on a routine basis with these instruments.

Radiocarbon Laboratory

I had hoped to see the radiocarbon laboratory but I was informed that it was not operational and it appeared that they were not anxious to have visitors when the equipment was being repaired.

École Nationale Supérieure de Géologie Appliquée et de Prospection Miniere, Université de Nancy

The Centre de Recherches Radiogéologiques under the direction of Dr. R. Coppens is housed in new laboratory buildings located on the hillside overlooking the ancient city of Nancy. I was received by Dr. G. Durand, who is in charge of the mass spectrometry and isotope work. In addition, I had the pleasure of meeting Mr. Govindaradju in charge of the spectrographic laboratory, Mr. Jurain, who has been operating a mobile radon detection laboratory, Mr. Richard, in charge of radiocarbon dating equipment, Mr. Sonnet, Rb/Sr age determinations and Mr. Kaplan, K/Ar age determinations.

Solid Source Analytical Techniques - Activators

Dr. Durand, assisted by Mr. Kastolanyi, has been developing a technique whereby lead, uranium and thorium ion currents may be analyzed simultaneously in the mass spectrometer. The process involves the preparation of an activator which is placed on the tungsten ribbon filament along with the sample of galena, pitchblende or zircon. The procedure is as follows:

> 1.2 gms $Na_2SiO_3.5H_2O$ is dissolved in 5 ml H_2O
>
> 1.4 gms $Zr(SO_4)_2.4H_2O$ is dissolved in 5 ml H_2O
>
> Mix solutions, let stand, decant, rinse with 5 ml of 10% H_3PO_4 and then afterward add 5 ml 10% H_3PO_4.

Special precautions must be taken in depositing the activator and the pitchblende on the filament in order to ensure the best results. The filament is heated to between 100° and 200° C., by passing a current through the tungsten. A platinum wire is used to apply a layer of the activator to the filament surface and this is allowed to dry slowly. A second layer, comprising a mixture of activator and pitchblende is deposited. When this is dry the colour of the surface may vary from grey to black depending on the quantity of pitchblende added. It has been found that an excess of pitchblende does not improve the emission of ions. The pitchblende-activator mixture is prepared on a watch glass or in a small quartz crucible by mixing two drops of activator and a fraction of a mgm. of pitchblende. The final quantity of pitchblende placed on the filament is a small fraction of this, and the actual quantity of lead on the filament amounts to a fraction of a microgram.

Dr. Durand reports that this quantity of lead is sufficient to produce ample ion currents over a period of many hours, and he has found that a sample which had been continually analyzed for many hours yielded a Pb^{207}/Pb^{206} ratio with less than ±1% variation throughout the run. It is estimated that the activation technique increases the emission by a factor of 1000. This increase is undoubtedly due to the enormous increase in the surface area of the tungsten filament as illustrated by photomicrographs which have been made of the filament surfaces before and after treatment.

Sensitivities comparable to that reported here have been obtained using boric acid flux with lead samples, however the real advantage to be realized through the application of this technique stems from the fact that no chemical pretreatment of the mineral is necessary. Samples of pitchblende, galena, and zircon, have been placed directly on the filament and the ion currents recorded. An additional advantage is that it is possible to record the ion currents of Pb, U and Th in the same sample without introducing new material to the mass spectrometer.

While Dr. Durand has been successful in producing satisfactory ion currents, he has not solved the problem of introducing enriched spikes to permit the determination of the concentration of the elements in the sample. It may be necessary to introduce at least one chemical step in the sample pretreatment to permit the intimate mixing of the sample and spike materials before they are applied to the filament.

The most successful analyses have been carried out by applying the activator to tungsten filaments. No apparent advantage was observed when the activator was used with rhenium filament material. Particular care must also be exercised in the preparation of zircon concentrates since thallium ion currents have been observed in the lead mass range. This contamination is apparently introduced when Clerici solution is employed during mineral separation procedures.

The method outlined above is being applied to detailed studies of pitchblende from the Black Forest region. Preliminary studies using gaseous mass spectrometric techniques, and consequently large samples, (approx. 10 mgm) yielded ages ranging from 265 to 60 m.y. with values distributed through the complete range. It was apparent that the results were a reflection of the fact that the large samples were mixtures of pitchblende of various ages. This is to be expected since some secondary uranium minerals have been found at depth, indicating extensive movement of both uranium and lead. In addition, some of the pitchblende age results were found to fall on the 'high' side of the 'concordia' type plot indicating an enrichment in uranium subsequent to original deposition. To overcome this difficulty, very small samples representing individual phases of pitchblende are being selected microscopically, and are to be analyzed isotopically by means of the activation technique.

K-Ar Age Determinations

The potassium-argon extraction apparatus, built by Mr. Kaplan, comprises a large extraction line permanently connected to a Thompson-Houston mass spectrometer of French manufacture. A high frequency induction heater is employed to fuse the micaceous samples which are placed in an iron crucible which acts as an inductor. The slag remaining, after the fusion, is drilled out and the crucible used for subsequent fusions. The electromagnetic coupling between the coils and the iron crucible must undoubtedly be very good but one must be careful not to exceed the melting point of iron at approximately 1500°C.

The extraction line is very large and it embodies many stopcocks. In addition the argon 38 spike stock is metered from a large volume through normal glass stopcocks. The purified gas is admitted directly to the source of the mass spectrometer and pairs of argon ion currents are recorded simultaneously by scanning electrostatically (the instrument is equipped with a permanent magnet). The analytical method involves the detection of first argon of mass 40 and mass 38 and subsequently mass 38 and mass 36. The pairs of ion currents are electronically compared and the result of replicate scans displayed as individual peaks representing the difference in the isotopic composition. The integrated result of this display is used in the calculation of the isotopic abundances. I was advised that using these techniques they have been successful in reducing the experimental error to a surprising low value. Mr. Kaplan claims to be able to reproduce ages of 500 m.y. within ± 1 m.y. I was not able to ascertain whether this very low error included the uncertainties introduced through the determination of the potassium content etc., or whether it reflected only the reproducibility of an individual mass spectrometric analysis of one gaseous sample. Even if the latter is correct the error is still surprisingly small.

Rb/Sr Age Determinations

The rubidium-strontium age determination work is under the supervision of Mr. Sonnet. The techniques employed are essentially those developed at the University of Clermont-Ferrand and they will be described in detail in the next section of this report. The analyses are carried out on an A.E.I. M.S. 2 mass spectrometer which had been modified to permit the analysis of solid samples. From an examination of the recorder output it was apparent that the instrument was not operating at maximum efficiency and that the recorder was not reaching the tops of many of the peaks and consequently the results would not truly reflect the isotopic constitutions of the sample.

Radiocarbon Laboratory

The radiocarbon laboratory was of conventional arrangement employing CO_2 as a counting gas. A great deal of trouble had been experienced with noise apparently originating in the capacitor in the input. A suggestion that the preamplifier be relocated inside the cosmic ray shielding has apparently been responsible for a marked improvement in the operation of the equipment.

The geiger tubes used in the anticoincidence arrangements are fabricated in France and are relatively cheap costing only $10.00 per tube. The address of the manufacturer is included in the appendix.

Radiocarbon intercalibration studies are being carried out on wood from a Birch tree burned by a lava flow in the Central Massive region of France. This material has been dated at 6000-7000 years.

Spectrographic Laboratory Air-Conditioning

Mr. Govindaradju supervises a very well equipped spectrographic laboratory. An ARL spectrophotometer is located in a specially designed air-conditioned laboratory complex comprising a room-within-a-room. The spectrographic laboratory, entrance to which is possible only by means of a special double door vestibule, is situated in the centre of the building with sample preparation areas and corridors between the laboratory and the outer walls of the building. It has been found that this peripheral area provides an excellent buffer between the laboratory and the atmosphere and hence temperature fluctuations are held to a minimum. In addition to the room control, an air-conditioning unit is built into the spectrograph cabinet. This unit is designed to control the cabinet area to within ± 0.1°F. and I was informed that they have experienced no difficulty in realizing this condition.

Université de Clermont, Clermont-Ferrand, France.

The visit to the age determination laboratories under the direction of Professor M. Roques was indeed most pleasant. His assistants Messieurs Yves Vialette and Michel Bonhomme kindly described all aspects of their operation to me. In addition, my visit fortunately coincided with a visit to the laboratories by Dr. Fransico Mendes of Lisbonne, Portugal. Dr. Mendes has completed arrangements to purchase an A.E.I. M.S. 2 mass spectrometer which he plans to install in the Laboratoris De Mineralogia, Faculdade De Ciencias in Lisbonne, where an age determination laboratory patterned after the Clermont group is to be established.

The laboratory under Professor Roque has served as a training centre for young scientists interested in isotopic age measurements. Mr. Bonhomme has set up a laboratory in Strasbourg, equipped with an A.E.I. M.S. 2 and an Atlas CH_4 instrument, where he will be in charge of age measurements. A group, similarly equipped, is being brought together to work under the direction of Dr. Mohamed Diouri, Chief of the Geological Service of Moroco, in Rabat.

Mass Spectrometric Apparatus

The Clermont laboratories are equipped with an A.E.I. M.S. 2 mass spectrometer which has been modified for solid source analyses through the addition of a vacuum lock and the introduction of a triple filament, solid source assembly. The instrument, with which all Rb and Sr analyses are carried out, was not operative during my visit due to difficulties arising in the eleven-stage electron multiplier. The gain of the multiplier had changed from about 50,000 x to 500 x over a period of 6 months and a replacement assembly was being installed. The vacuum lock arrangements apparently operates very rapidly and it is only necessary to wait about 10 minutes between analyses.

A second mass spectrometer with a 9" radius 60° deflection analyser tube was being constructed at Clermont. An A.E.I. source assembly has been incorporated in the home design. The group plans on the extention of their work to include K/Ar age measurements and this instrument is to be used exclusively for the necessary argon analyses.

Rb/Sr Age Determinations

The experimental technique employed in Rb/Sr age determinations is outlined in the following.

Sample size = 0.5 gm biotite, muscovite or whole rock

= 0.1 gm of lepidolite.

Sample + 15 c.c. HF + 3 c.c. $HClO_4$

Take up in 1N HCl

Make up to a volume of exactly 50 c.c. - Solution A.

1 c.c. of solution A + 1 c.c. of Rb spike = solution Rb1A

1.c.c. of solution A + 1 c.c. of Rb spike = solution Rb1B

Each mixture is evapourated to 0.5 c.c. and sent to the mass spectrometer for isotopic analysis.

20 c.c. of solution A + 2 c.c. Sr spike

Evapourate to dryness

Take up in 2 c.c. of 2.5 N HCl

Centrifuge to separate perchlorates.

Solution transferred to ion exchange column (9 mm diameter x 20 cm long, containing Dowex #50, 8% cross linked, 100-200 mesh). Elute with 70 c.c. of 2.5 N HCl.

Collect strontium in the 70-85 c.c. fraction

Evapourate to dryness

Take up in HNO_3 - solution Sr 1 A

Repeat on separate fraction to produce - solution Sr 1 B

Mass spectrometric analysis carried out on Sr NO_3.

By combining the results from solutions Rb1A, Rb1B, Sr 1 A and Sr 1 B, four ages may be calculated. This complete procedure is repeated three times on separate fractions of the same sample and a total of twelve age measurements are determined. The twelve figures are then averaged and the error calculated to obtain the limits of the 95% confidence interval ($\sim$ 2 x standard deviation) which is then used in the geological interpretation of the data.

The procedure outlined above is extremely time consuming, especially when one considers that a total of six Rb and six Sr mass spectrometric analyses are required to complete a single determination and that a minimum of three complete determinations are essential to establish a single whole rock isochron.

The chemical procedures have been set up on a production line basis, and young women have been trained to carry out the routine processing. All work is performed in an open laboratory and no particular attempt is made to prevent the introduction of contamination, etc. The 12 results of one biotite determination that I was shown ranged from 322 m.y. to 360 m.y. with a mean of 344 m.y. and this had been assigned a 95% confidence level of ±8 m.y., or approximately ±3% of the age.

In the majority of laboratories involved with this type of work it has been noted that the major time-consuming bottleneck is attributable to the mass spectrometric analysis, and consequently scientists have been striving to reduce the number of instrumental analyses required per age determination. In order to realize this goal greater effort has been put into refinements in the chemical processing procedures, particularly with regard to precautions designed to reduce the contamination originating in reagents and laboratory air. By monitoring the levels of contamination by means of blank runs, it has been found that single Rb and Sr determinations are usually sufficient. However in particular cases, as for example very young samples or samples with a high total Sr/Rb ratio, duplicate analyses based on different ratios of sample to spike solutions are employed. When such precautions are taken one usually finds that the Rb and Sr concentrations agree within a maximum limit of ± 3%.

Professor Roques has set up a very detailed system to control the flow of samples from the crushing laboratory to the chemical laboratory and finally to the mass spectrometer laboratory, and in spite of the large number of determinations required per age result, the laboratory has completed more than 600 Rb/Sr analyses.

M. Yves Vialette has applied the technique to a detailed study of the granite massive, Le Sidobre. Age measurements have been carried out on micas from the two phases of the batholith and from the metamorphic aureole surrounding the granite. He has shown that there is no significant age difference between samples from the granite and from the metamorphic zone and that the average age is 290 ± 6 m.y. He has also shown that while the Rb concentration varies somewhat between the two phases of the granite, the strontium concentration is quite constant.

In addition, detailed studies of micas and whole rock samples from the principal granitic and migmatite formations of the Massive Central indicate the existence of three successive periods of migmatization and six periods of granite formation. These range from the oldest migmatites which fall between 680 m.y. and 560 m.y. and the youngest at 290 m.y.

M. Michel Bonhomme has carried out a detailed study of the geochronology of the basement rocks of East Africa and has distinguished four principal phases of metamorphism and granitization in the following age ranges, 2600 m.y., 2030-1830 m.y., 580-510 m.y., and 330, 230 and 180 m.y.

Mineral Separation

A floatation device is employed for biotite separations. The apparatus consists of a glass tube about 48" long and 2½" in diameter fixed to the top of an erlenmeyer flask, and having appendages at various heights to permit the introduction of the sample and the removal of concentrates.

The ground sample (less than 80 mesh) is put into the column through a funnel at the top and the water enters the flask at the bottom. The water flow is adjusted to carry the mica flakes up the column and out through a hose attached near the top. They then settle in a beaker in the sink. The feldspar concentrate is removed via a stop cock in the lower region of the tube while the zircons and other heavy minerals collect in the erlenmeyer flask. This arrangement appeared to work very rapidly and I was informed that approximately 15 minutes was generally sufficient to complete the separation.

A paramagnetic separator is employed to remove quartz, feldspar and muscovite from the biotite concentrate. This unit, known as an Analyseur de Paramagnetique (Forrer) is manufactured by Electrona, Lingolesheim, Bas-Rhin, France and costs about $1000.00. Muscovite concentrates are then purified in bromoform.

Pictures of the flotation equipment and the paramagnetic separator are on file in the Isotope and Nuclear Geology Section.

Fission Age Measurements

An interesting method of age measurement based on the observation of fission damage tracks in phlogophite is being studied. If samples of phlogophite having flakes about 10 microns thick are treated in HF and then washed and placed on a microscope slide one may observe fission damage tracks up to 14 microns in length.

The procedure employed to determine the age is as follows: The fission damage tracks in a known volume of the sample are counted after the initial treatment in HF. The sample is then irradiated in a neutron flux and the damage tracks produced by the neutron induced fission are counted to provide a measure of the uranium concentration in the sample. One then uses the spontaneous fission λ of 10^{-15} to 10^{-17} yrs^{-1} to calculate the age of the mica.

They report that fission damage tracks have been observed in phlogophite, muscovite and lepidolite after treatment in HF for 15-30 sec., 10 minutes, and 2-3 seconds, respectively.

4. Italy

Instituto Di Geologia Dell Universita, Pisa

The visit to the Institute of Nuclear Geology, directed by Professor Ezio Tongiorgi, was arranged through Professor G. Dessau, also of the University of Pisa. It was my privilege and pleasure to spend considerable time with Professor Dessau whose kindness helped to make my visit a most memorable one.

The laboratories are housed in a very old four story building situated on the main street leading to the famous Leaning Tower of Pisa. The contrast between the very old surroundings and the modern scientific equipment, filling every available bit of space, is most striking.

The Institute of Nuclear Geology is apparently the primary Italian laboratory carrying out isotopic studies and is consequently rather well financed. There appeared to be no shortage of apparatus. The laboratory is equipped to carry out age measurements based on Rb/Sr and K-Ar ratios, studies of stable oxygen and carbon isotope variations, C-14 age determinations, Pb-α age measurements, and spectrographic studies. In addition to Professor Tongiorgi I had the pleasure of speaking with Drs. G. Farrara, A. Longinelli and R. Gonfiantini.

Mass Spectrometric Apparatus

The Institute has five mass spectrometers including one Atlas CH_4 unit used for Rb and Sr analyses, two Atlas M86 units designed for rapid comparison of gaseous samples, one home constructed 60° instrument also designed for rapid gas analyses, and a Reynolds type tube for argon age determinations.

The Atlas CH_4 instrument is fitted with a vacuum lock and a double filament source for the analysis of solids. This was the first instrument of this type that I saw being used for Rb and Sr analyses although I was to be shown others in laboratories in Bern and Hannover. The instruments appear to be ideally suited to this type of work and all scientists using them are most enthusiastic about their performance and reliability.

The Atlas M86 instruments were especially designed for the simultaneous collection of two ion beams to facilitate the precise determinations required for palaeotemperature studies. Both machines are fitted with all metal sample handling lines embodying Atlas metal values. These appear to work very rapidly and are quite trouble free. The recorder traces were very stable and the sensitivity for CO_2 was such that a displacement of 1 cm was equivalent to an isotopic difference of approximately 1.5 ‰.

The Reynolds glass analyzer tube is being set up for use in conjunction with the argon extraction apparatus and will be used exclusively for the analysis of radiogenic argon extracted from minerals and rocks.

K-Ar Age Determinations

A new argon extraction line was being set up at the time of my visit. The apparatus is to include a very large Philips 12KW induction heater. Several samples, each weighing approximately 200 mg., are put in small aluminum crucibles and placed inside the vacuum chamber. When a sample is to be fused, the aluminium crucible and sample are dropped into a molybdenum crucible which serves as an inductor in the field of the high frequency coil. In this manner several samples may be fused without opening the reaction vessel to the atmosphere. A new molybdenum crucible is installed after each group of fusions.

All argon concentrations are carried out using Ar^{38} spikes made up from the European produced enriched argon-38 stock (99.8% argon-38). The individual spike tubes are very large (25 mm. diameter) and each contain approximately 10^{-4} c.c. at S.T.P. All spike tubes volumes are determined by filling them with purified mercury.

Dr. G. Farrara plans to carry out detailed K-Ar age work on many of the younger volcanic formations of Italy.

Rb-Sr Age Determinations

In order to accurately determine the radiogenic Sr^{87} concentration it is essential that the common Sr content of the samples be kept as low as possible. At Pisa, Dr. Farrara has designed a special laboratory equipped with air filters and he has incorporated various safeguards to reduce common strontium contamination which may be introduced via chemicals and through excessive human traffic in the sample handling area. In addition, following treatment on Franz separators, the mica concentrates are placed in a special agate mortar with alcohol. This grinding procedure separates the biotite flakes thus liberating impurities which may then be removed. It has been shown that these impurities are the primary source of common strontium.

The mica concentrates are dissolved in a mixture of HF and $HClO_4$ and one third of the solution is used for the rubidium determination while the remainder is retained for the determination of the strontium concentration. The first portion is evaporated to dryness, taken up in HCl and spiked with the Rb tracer solution. RbCl is used for the mass spectrometric determination.

The remainder is spiked with the Sr tracer and placed in a centrifuge to bring down the K and Rb perchlorates. The solution is placed on an ion exchange column (along with a Sr 89 radioactive tracer) in order to separate the remaining Rb from the Sr. The ion exchange columns are discarded after each sample is processed.

The fraction containing the majority of the strontium is treated with perchloric acid, to destroy particles of resin, is evapourated to dryness, taken up in a few drops of nitric acid and is then placed on a previously outgassed filament. A current is passed through the filament to evapourate the excess moisture. A drop of ammonium oxalate is then placed on the filament. The sample apparently converts to SrO_2 when heated in the mass spectrometer and with this arrangement Dr. Farrara reports that he obtains steady ion emission with from 0.5 to 1.0 micrograms of sample. Unfortunately, considerable difficulty is experienced with power line fluctuations in Pisa and Dr. Farrara finds it is difficult to obtain the most acceptable checks between replicate analyses. The best results, to date, have been found to agree within ±2%.

Oxygen and Carbon Isotopic Studies.

Drs. R. Gonfiantini and A. Longinelli are responsible for studies of palaeotemperatures based on oxygen isotope measurements and for carbon isotope investigations. As noted previously, they have at their disposal, two Atlas M86 dual collector mass spectrometers. I was informed that Dr. Harmon Craig of Scripps Institute of Oceanography at La Jolla, California had spent eight months at Pisa during 1962-63 and that he had assisted them in setting up the necessary apparatus.

Dr. Longinelli hopes to refine the procedures required for the measurement of palaeotemperatures based on the study of phosphates. This work was pioneered by Dr. A. Tudge who found that it was possible to overcome the uncertainty introduced in the temperature estimations due to the lack of knowledge re the oxygen isotope ratios in sea water in Quaternary time. Dr. Longinelli feels that many of the palaeotemperature measurements may be in error as a consequence of this uncertainty.

Radiocarbon Dating Laboratory

The apparatus required for C-14 dating had been set up in Pisa but it appeared to have been neglected in recent months and was not operating at the time of my visit. The counter tube was made of stainless steel and it was fitted with glass ends through which a series of electrical lead-throughs had been placed. Two sets of wires, positioned concentrically about the central wire, were attached to these lead-throughs to provide the anti-coincidence ring which is usually made up of a series of geiger tubes placed around the outer circumference of the counter tube. The central counter and the area around the concentric wires is filled with the sample gas and all are operated in the proportional range. They have been converting the samples to acetylene and find that this arrangement has a background count of 1.57 c/m when operated at one atmosphere pressure. The laboratory also has an Oescheger type (made in Bern) tube but this was not positioned within the cosmic ray shield when I was there.

Miscellaneous Apparatus

In addition to the mass spectrometic and vacuum apparatus used for isotopic studies the laboratory was equipped with a 128 channel pulse height analyzer used for some Pb-α age measurements and for U-Th disequilibrium studies. They are also interested in determining certain trace elements in artifacts and have set up a new ARL grating spectrograph to facilitate the determinations.

5. Switzerland

Mineralogisch-Petrographisches Institut, Universität Bern

Undoubtedly the most interesting visit of the entire schedule was spent in Dr. Jäger's laboratory in the Mineralogisch-Petrographisches Institute at the University of Bern. Dr. Jäger has developed the techniques required for precise Rb and Sr determinations and has applied them to the measurement of very young materials. The extent of her success in this field of endeavour may be judged from the observation that scientists in all European institutions have either visited her laboratory or are planning to do so.

Dr. Jäger's primary interest has been in the Rb-Sr age determination field, but she is now assembling the apparatus required for K-Ar age measurements.

The laboratories, including a mineral separation laboratory, a chemical laboratory and a mass spectrometer laboratory are now located in the Institute at Sahlistrasse #6. During the early stages of the work Dr. Jäger did not have a mass spectrometer at her disposal and all isotopic analysis were carried out on instruments in the Physics Department of the University of Bern in another section of the City. The laboratory now has an Atlas CH_4 solid source instrument and I was informed that plans are being completed for the purchase of a second identical unit.

Dr. Jäger has one full time technician operating the mass spectrometer and part-time assistance of a chemist. She collects all of her materials in the field and supervises all aspects of mineral separation, chemical processing and data calculation.

Mineral Separation

The Sr^{87} concentration of a smaple is made up of a common strontium component (7% of total strontium) and a radiogenic component produced through the decay of Rb^{87} in the sample. The radiogenic contribution is a function of the Rb^{87} concentration and the age of the material. In order to facilitate the accurate measurement of the radiogenic component in young minerals it is essential that the common Sr content be kept to the lowest possible level. Dr. Jäger has demonstrated that dust is a major contribution of common strontium and she has designed elaborate exhaust hoods that are placed over all of the machines used in the mineral separation operations.

The initial crushing and grinding are carried out in one room and the final mineral concentrates are prepared in the cleaner mineral separation room. The sample is only ground fine enough to release the micas as single flakes. After sifting several times, under strong air suction, the coarser sieve fractions are taken to the final separation room where the concentrate passes over a shaking table of the type described by Faul and Davis (Am. Mineralogist, 44, 1076-1082, 1959). Only the fraction of perfect flakes remaining is used for further purification. Following magnetic separation with a Franz separator the flakes are ground in an agate mortar in alcohol. This grinding bends the flakes and the alcohol helps to separate them. After 10-20 minutes the majority of the intergrown grains and inclusions containing Sr-rich apatite grains will fall out. The final concentrate is washed several times in alcohol until it has a dust free, bright surface. No water is used at any time since it has been observed that the micas are often stained after water treatment.

The finer fractions produced in the initial grinding are passed over the Wilfley table to concentrate the zircons.

Rb/Sr Age Determinations

All chemical extractions are carried on in a small laboratory that must be entered through another laboratory. Special air filters are used to purify the air admitted to the room and an electrostatic filter is used for the air taken into the fume hood. The air blown into the hoods forms a curtain to prevent the movement of room air through the hood. The hood is made of wood and is lined with 4 mm. thick sheets of polyvinylchloride which is resistant to perchloric acid fumes. Table tops are plastic and the walls and fixtures have been painted with lead-free paint. All reagents are redistilled or recrystallized and all evapourations are carried out in teflon or silica vessels.

In order to correct the strontium isotopic analyses for instrumental discrimination introduced during the analysis the samples are all spiked with a solution containing both enriched Sr^{84} and Sr^{86}. This technique is referred to as 'double spiking'.

The chemical procedure is as follows:

Sample (0.5 gm) + double Sr spike (by weight)

Add 2 ml HF + 100-110 drops $HClO_4$

Evapourate to dryness.

Put in 100 ml. pyrex flask and make up to 100 ml with 1.5 N HCl.

Weigh.

Take approx. 1 gm. of solution and place in Teflon vessel

Add approx. 1 gm. Rb spike (or Rb + K spike if K determination to be made at the same time).

Evapourate to dryness.

Add a drop of 8% H_2SO_4.

Place on Ta mass spectrometer filament (see mass spectrometry following).

Take approx. 50 ml. of solution remaining in 100 ml. flask.

Place in quartz crucible.

Evapourate to dryness.

Take up in 2 ml. of 2.5 N HCl.

Centrifuge to precipitate K, Ca, and Rb perchlorates.

Place 2 ml. on ion exchange column.

See section following on procedures followed with respect to column.

Evapourate portion from column containing Sr to dryness.

Destroy resin with $HClO_4$.

Evapourate to dryness.

Add a drop of HNO_3.

Place on Re mass spectrometer filament (see mass spectrometry following).

Ion Exchange Columns

The columns are made of 1 cm. O.D. pyrex glass and have a fritted disk mounted about 5 cm. above the lower, tapered, end. The tubes are filled, to a depth of 18 cms., with resin type Ag-50W-X8, 200-400 mesh, hydrogen form. A female standard taper joint is attached to the top of the tube to facilitate the use of a 100 ml. flask or a special adapter employed to resettle the resin between runs.

The techniques employed for Sr purification are as follows:

The 2 ml. portion containing the Sr is placed on the column. (Care must be taken to prevent the liquid from touching the inner walls of the column above the surface of the resin as it has been noted that Rb tends to remain on the walls and subsequently comes through the column in the later fractions thus contaminating the Sr portion.)

Wash down the walls with 1 ml 2.5 N HCl.

Put 12 ml. of 2.5 NHCl in column - let all run through.

Put 50 ml. of 2.5 N HCl in column - let all run through.

Put 13 ml. of 2.5 N HCl in column - collect for Sr cut.

No radioactive Sr tracer is used.

Let column drip until all acid has run out.

Flush with 5 column volumes of 6 N HCl.

Resettle column twice to prevent formation of canal ways.

Mass Spectrometry

An Atlas CH_4 mass spectrometer is employed for all isotopic analyses. Samples are mounted on the centre filament of a standard Atlas double filament assembly. The side filament in this case being used to help evapourate impurities from the material on the central ionizing filament. The source assemblies are previously outgassed in the mass spectrometer to ensure that no impurities are present in the mass range to be studied.

Rubidium samples (as Rb_2SO_4) are placed on tantalum filaments, care being taken to distribute the sample over the whole surface of the filament in order to prevent the emission of impurity ions from the tantalum surface. Tantalum ribbon is favoured for Rb analyses because the Rb blank contribution has been found to be about 1/20 of the amount found in rhenium ribbon. If both Rb and K analyses are to be carried out on the sample the K analysis is completed before the Rb is analyzed.

Strontium nitrate is placed on a tantalum filament and heated to a dull red heat on the bench. This procedure expels the majority of the Rb remaining, and converts the sample to strontium oxide which produces the most stable ion emission. Ammonium oxalate is not added to the filament.

Analyses are not continued until the material is exhausted but are terminated as soon as a sufficient number of reliable scans have been recorded. This precaution serves to prevent the excessive build up of sample material on other parts of the source assembly.

K-Ar Age Determinations

The age studies are to be expanded to include K-Ar age measurements and preliminary plans are being made to fuse the micaceous concentrates in a high pressure vessel. If this technique proves practical it will eliminate the necessity of installing a high frequency generator of the type employed in our laboratory

Physikalisches Institut - Universität Bern

A very brief visit to Professor Houtermans' laboratory in the Physical Institute at the University of Bern was conveniently arranged by Dr. Jäger. Unfortunately, due to illness, Dr. Houtermans was not at the laboratory but in his absence Dr. J. Geiss very kindly received me. The mass spectrometric section is well equipped with both Atlas Werke and home designed mass spectrometers. The common lead isotopic studies, originally pioneered by Dr. Houtermans, appeared to have been superseded by research on meteoritic materials. Conventional, high vacuum fusion and gas purification apparatus has been assembled to process rare gases found in meteorites.

Dr. H. Oescheger has set up a radiocarbon and tritium laboratory in the basement of the Institute. I was shown a C-14 proportional counter arrangement of the "Oescheger" design having an active volume of 1.5 litres and a background count of 0.6 c/m at a pressure of one atmosphere. All radiocarbon samples are counted in the form of CH_4.

Dr. Oescheger is currently transistorizing all of the electronic units used in the C-14 and tritium work. The latter technique is being applied to studies of materials from cores taken from the Greenland ice cap. It is of interest to note that a portion of a World War I gun barrel was being used to provide the necessary shielding for one of the tritium counters.

E.T.H. Mineralogical Institute - Zurich

Fortunately I was able to arrange a visit to Zurich where I learned of Professor Marc Grunenfelder's detailed zircon studies. Large concentrates ($\sim$ 1 gm) of two types of zircon, one clear and the other turbid or milky, have been separated from a granodiorite from Acquacalada and have been subjected to trace element and isotopic investigations. The two types are considered to be cogenetic since both clear and turbid material has been observed within a single crystal.

The two types of zircon have been found to possess strikingly different features. Both were fused in borax and the lead and uranium were extracted, for isotopic analysis, using the techniques developed by

G.R. Tilton. The turbid variety fused in about 10 minutes whereas one hour was required to completely fuse the transparent fraction. Isotopic analyses were carried out by Dr. Jäger in Bern and X-ray micro probe studies were handled in Geneva, using an ARL instrument. The milky zircons contained about three times as much uranium as the clear variety, and in addition yielded a younger U-Pb age of 210 m.y. as compared with the U-Pb age of 320 m.y. determined for the transparent type. The older age agrees with the age measured for other suites of transparent and homogeneous zircon families found in other granitic masses in the same tectonic unit. The younger age (210 m.y.) found for the turbid zircons is undoubtedly due to intergranular transformations which have taken place during the lifetime of the crystal and consequently the U-Pb ratio has been affected by a disturbance of the radioactive equilibrium. Both varieties have been affected by a recent metamorphism (indicated by biotite Rb/Sr ages of 15-16 m.y.) and the transparent zircons appear to have retained their radiogenic lead whereas the turbid variety have lost a portion of their lead, either as a result of continuous diffusion or a single episode.

In addition, microprobe analyses have revealed that the uranium, hafnium and zirconium distributions in the clear zircons are homogeneous while in the case of the milky crystals the hafnium is concentrated at the crystal boundaries.

Professor Grunenfelder feels that the high uranium concentration alone cannot explain the age discrepancy since there is no other evidence for uranium gain. Rather he postulates that the high water content and inhomogeneous distribution of uranium and hafnium in the turbid zircons has been responsible for the disturbance of the radioactive equilibrium.

He has also observed that the turbid zircons generally made up the smaller sized fractions and as L.T. Silver has noted they contain most uranium, and yield the most discordant age results. It is obvious that detailed studies of the chemical and physical properties of the zircon suites is essential if a meaningful interpretation of the age results is to be realized.

6. Germany

Max-Planck-Institut Für Kernphysik, Heidelberg

The Director of the Institute, Dr. W. Gentner, was unfortunately away from Heidelberg and consequently I did not have the pleasure of making his acquaintance. However, I am indebted to Drs. Zähringer and Lipholt for a most interesting visit.

Detailed studies of the rates of diffusion of argon from various terrestrial materials, and the rare gas content of tektites, and of meteorites are being carried out. Samples are fused in vacuum, using apparatus similar to ours and the gases released are analyzed mass spectrometrically. A mass spectrometer is permanently attached to each of the extraction lines and analyses are carried out immediately after fusion of the sample. Isotope dilution techniques are employed to determine the elemental concentration of the released gases.

The laboratory is equipped with several home designed 60° mass spectrometers featuring both glass and metal analyzer tubes, and in addition, an Atlas CH_4 unit has been installed. The latter instrument is employed primarily for the isotopic analysis of solid samples, particularly lithium samples.

A simple method is employed to meter the enriched isotopic samples required for the isotopic dilution of the released gases. This comprises a calibrated volume in the form of an inverted glass U tube, mounted so that the ends may be sealed by raising the level of mercury in the appropriate chamber. One pipette is used for each of the enriched gases (He, Ne and Ar) and each is connected to a 5 litre volume containing the stock of enriched gas. The pipette volume is such that several hundred portions may be extracted before the pressure in the reservoir is appreciably reduced. A considerable saving in time may be realized with this method of spike control and plans are now being made to incorporate the system in the G.S.C. argon extraction apparatus.

Argon Diffusion Studies

Radioactive Ar^{37} and Ar^{39} have been used to measure the diffusion of argon in natural samples of sanidine, phonolite, augite, a Bohemian tektite and a synthetic sylvite. The straight line relationship between $D/_{a}2$ vs $^{1}/_{T}$ found for the tektite and the sanidine is taken to represent a volume diffusion mechanism, whereas diffusion from lattice imperfections has been postulated to account for the results obtained for the phonolite and augite. The values of $D/_{a}2$ for volume diffusion at room temperature for the materials studied are so small that K-Ar ages for these do not require correction. However, diffusion from lattice imperfections may be significant. The investigation verified that sanidine and mica are the best materials for K-Ar age measurements whereas other feldspars and rocks are not as suitable. Also salts may only prove reliable in exceptional circumstances.

K-Ar Age of Tektites

A large number of tektites have been dated by means of the K^{40}-Ar^{40} ratio. These have been found to fall into three very distinct groups as follows: all North American tektites - 34 m.y.; all Czechoslovakian tektites (moldavites) - 15 m.y.; Indo-China - Australia - 0.6 m.y. and a fourth group based on two samples from the Ivory Coast at 1.3 m.y. All of the ages agree with the ages of the formations in which the tektites have lain. This fact alone, indicates a terrestrial origin for the tektites and, in addition, samples containing bubbles have been found to contain gases having isotopic abundance ratios identical with terrestrial gases.

K-Ar age of Limestones and Fluorites

Dr. Lippolt has attempted to employ the K/Ar method to date limestones and fluorites. In the former case he found some promise of reliable results but in the latter case the calculated age was found to be much too high. Grinding of the samples tended to reduce the indicated age but this process also reduced the K value. It is believed that the potassium exists in the inclusions and this K contributed to radiogenic argon which was released from bubbles when the sample was finely ground. In addition to the radiogenic argon a large atmospheric component was observed. It is postulated that this atmospheric argon was incorporated into the minerals when they formed in the hydrothermal veins.

Rare Gas Adsorption Experiments

Preliminary results of experiments designed to test the possibility of absorption of rare gases in chondritic material were available. The following technique was used to determine the absorption of He, Ne and Ar in silicate melts. The material was held at 1700°C. for 60 minutes in an atmosphere of the rare gas. The sample is then cooled to 20° C. in one minute. The absorbed gas is then released by fusing the sample and the amount absorbed is determined mass spectrometrically. Results obtained to date, indicate that the He absorption is a linear function of the pressure, Ne is absorbed in an erratic fashion but the total amount absorbed is comparable to the quantity of He taken up. However, the Ar absorption was found to be very low and essentially independent of the gas pressure, up to one atmosphere. This work is to continue and is to be extended to embody a study of the absorption characteristics of Kr and Xe.

Laboratory Apparatus

The laboratory was also equipped with a microprobe analyzer, of French manufacture, which I was told was operated routinely. While I was there a new Philips X-ray Diffraction instrument was being installed. The electronic units for this equipment were of the latest, completely transistorized design.

Radiocarbon Dating Laboratory

Unfortunately, only a very short time was available for a visit to Dr. K.O. Münnich's C-14 dating laboratory in the University of Heidelberg. Dr. Munnich was away sick but I was given a brief tour by one of his students.

All samples are converted to CO_2 for measurement and the majority of the work is carried out at two atmospheres pressure. They have apparently experienced considerable difficulty when attempting to operate the counters at pressures above 3 atmospheres. The background counting rate for one of the 2 litre proportional counters was 8 c.p.m. when operated at two atmospheres. One counter is located in the basement of the building at a depth of about 3M. This 2 litre unit has a background of 6 c.p.m.

The laboratory is also equipped with two Atlas mass spectrometers used for H/D, C^{12}/C^{13} and O^{16}/O^{18} measurements.

In addition to C-14 determinations work on tritium in natural materials is being undertaken. A glass column, 6 feet long is used to enrich the H^3 content of the gas samples before measurement. An enrichment by a factor of 10 is realized within one day.

Zentrallaboratorium für die Geochemie der Isotope, Göttingen

The laboratory, located on the campus of the University of Göttingen, is set up as a central German laboratory for the study of stable isotope variations, primarily sulphur at this stage, and their application to geological problems. Dr. Heimo Nielsen is the chief of the laboratory which has been established under the general direction of Professor C.W. Correns. The group receives support from an advisory board comprising prominent German scientists whose fields of specialization embrace geology, physics, and chemistry. The board, in consultation with the chief of the laboratory, discusses the technical aspects of projects proposed by scientists working in eduational organizations and industry. Provision is made to proceed with promising projects and the scientists concerned are invited to come to the Zentrallaboratorium to assist with the processing and analysis of their samples. Each scientist may visit at the laboratory for two or more periods of from 2 to 3 weeks duration. Schedules for the visits are prepared well in advance and it is the visiting scientist's responsibility to have his materials ready when he visits Göttingen. After a reasonable period has elapsed, during which the scientist has had an opportunity to compile and assess the experimental results, joint interpretation sessions are arranged with the laboratory staff.

Mass Spectrometer Laboratory

All sulphur analyses are carried out on an Atlas CH_4 mass spectrometer which, unfortunately, does not appear to be the most suitable model for this type of isotopic analysis. In spite of this, however, a second identical unit was being installed during my visit.

The Atlas CH_4 model is equipped with a low pressure molecular leak sample inlet system attached to a large (6 litre) sample reservoir chamber. The gas sample (SO_2) to be analyzed must first be expanded into the large volume and is then permitted to flow through the low pressure leak into the ion source chamber of the mass spectrometer. This type of arrangement has a very long time constant which prevents the rapid comparison of standard and unknown samples commonly realized with the high pressure viscous leak system employed in our laboratory. In addition the time required to pump the sample out of the 6 litre volume after the analysis has been completed is excessively long. Dr. Nielsen is now contemplating the installation of an arrangement identical to that of G.S.C. mass spectrometer No. 1.

Considerable difficulty has also been experianced with the high voltage supply used on the CH_4, which is apparently only stabilized with a voltage regulator tube. Consequently, the recorder trace is not stable when the two ion beams are being electronically compared. The problem has been partially overcome by introducing a measuring technique which essentially averages the data and yields a single point representative of the balance reading for each gas sample.

It has been observed that, after a large number of SO_2 analyses, a non-conducting layer builds up on the collector electrodes. To overcome this problem carbon rod has been fitted into the bottoms of the Faraday collectors. I have not encountered any other workers experiencing this particular difficulty.

Although simultaneous collection techniques are employed to measure the ion currents at mass 64 and 66, an additional refinement has been incorporated into the operational procedure, to permit the slow scanning of the smaller ion beam (mass 66) across the collector slit. This refinement in some measure compensates for the lack of stability in the high voltage supply referred to above.

As a consequence of the long time constant associated with the molecular leak system a period of 50 seconds is required between the introduction of gas samples being compared, and approximately 20 minutes is required per analysis. All analyses are carried out on a strict time schedule. A standard gas sample is first compared with an unknown gas, X, this is followed by a comparison of X, with a second unknown, X2, then X2 with X3, and so on until finally, Xn is compared with a sample of the original standard to complete the circle.

Sulphur Dioxide Preparation

Sulphur containing minerals (sulphides) are converted to SO_2 for isotopic analysis in batches of nine. Vanadium dioxide is employed as a source of oxygen with constant isotopic abundance. The sample to be converted and a portion of V_2O_5 are pre-baked, separately, under vacuum. They are then mixed and placed in quartz tubes prior to being baked at 300°C. under vacuum for a period of 12 hours. The quartz tubes are sealed and placed in an oven maintained at 1000°C. The reaction is complete after 15 minutes at this temperature and the gas is ready for mass spectrometric analysis. Sulphate samples are converted to CdS prior to the conversion to SO_2 as outlined above.

This technique would appear to be about as time consuming as the one currently employed in our laboratory. However, according to Dr. Nielsen this system is superior when one is required to convert very small samples.

A novel method is employed to transfer the SO_2 from the quartz tubes to the mass spectrometer. The sealed quartz tubes are placed in a teflon or tygon heavy walled tube which has been heat welded at the bottom and is attached to a standard taper glass joint. A piece of stiff wire is also placed in the plastic tube to ensure a passage for all the air to escape when it is evacuated on the mass spectrometer. A pair of pliers is then used to crush the tube and break the quartz vessel, thereby releasing the SO_2 for analysis.

Plans are now being made to use solid sulphur samples for isotopic analysis. The sample, in the form of AgS, is placed on a pure

Ag electrode. Sulphur atoms are released from the sample when a high voltage is applied across the sample and electrode. The sulphur atoms are permitted to migrate into the ionization chamber where positive ions are formed as in a conventional gas source mass spectrometer. Dr. Nielsen hopes to be able to analyze samples containing only a few micrograms of sulphur using this technique. The technique will not, however, lend itself to the rapid comparison of samples essential for the detection of very small isotopic differences.

Sulphur Isotope Variations

Investigation of the relationship of the S^{32}/S^{34} ratios found in sulphides and sulphates from the same deposits have shown that the variations are often much smaller than that expected for equilibrium deposition from the same hydrothermal solutions. In such cases it is postulated that the equilibrium is formed between sulphate and complex sulphide ions. When large differences are observed however, and especially when the S^{32}/S^{34} sulphate is highly enriched in S^{34} it is suggested that hydrothermal solutions containing dissolved caprock sulphate have been responsible for the formation of the sulphate.

Detailed studies of sulphides and sulphates in a single deposit formed in a shallow region of a Devonian ocean indicate that the differences are much smaller than would be anticipated for fractionation effects operating on material from the same source. The explanation proposed suggests that the two types of sulphur came from different sources. The sulphide sulphur from hydrothermal solutions probably in the form of complex ions and the sulphate precipitated from the sea. Since no fractionation results during sulphate precipitation, the barite has preserved the ratio of the isotopes in the Devonian ocean. This result agrees with and compliments Dr. Thode's exhaustive investigations of evapourite deposits which have been found to have preserved the sulphur isotopic ratio of the seas from which they have been precipitated.

Bundesanstalt Für Bodenforschung, Hannover

Fortunately it was possible to arrange a short visit to the isotope laboratories of the German Geological Survey. This group, under the direction of Dr. Immo Wendt, is located in an old three story house at Wiesenstrasse 33, a few steps from the survey headquarters building at Wiesenstrasse 1. The chemical laboratories associated with the group are situated elsewhere in the city and I was not able to visit them. It is anticipated that the laboratories will be united in new quarters within 18 months.

This group has developed along lines similar to other European organizations, in that they have become involved with Rb/Sr age determination techniques at the outset, and are now completing plans to set up apparatus required for K-Ar age measurements.

Mass Spectrometric Apparatus

As would be anticipated, this laboratory is also equipped with several Atlas Werke mass spectrometers. A very early version of the model CH_4 is used for Rb/Sr and Pb/U analyses. This unit embodies a double filament source assembly and a 14 stage electron multiplier having a gain of about 10^5. Some difficulty was being experienced with the apparatus due to drop off of ion current intensity during an analysis.

A new CH_4 instrument was being set up for oxygen and carbon isotopic analyses. The C^{12}/C^{13} ratio of gas samples prepared for C14 age measurements are to be determined and O^{18}/O^{16} palaeotemperature studies are proposed.

A third Atlas mass spectrometer is being incorporated into the argon extraction apparatus to be used for K-Ar age determinations. This latter equipment also embodies a Philips high frequency generator identical to our unit. A carbon crucible is to be used to fuse micaceous samples which may be dropped into the out-gassed vessel as required. A calibrated capillary is to be used to meter the Argon-38 spike material from a large (6 l.) vessel containing the spike stock. This arrangement is patterned after the system employed in the Max Planck Institute in Heidelberg.

I was informed that delivery of a fourth mass spectrometer (also an Atlas) was expected soon. This unit will be used for Pb, U and Th analyses, thereby reducing the pressure on the original instrument.

A 400 channel analyser (Victoreen) is used to determine the Pb^{210} activity. Data obtained is employed to augment the age calculations based on U-Pb and Th-Pb ratios.

Radiocarbon Dating Laboratory

Two proportional counters with active volumes of 2 litres and 3 litres are now in operation and plans are advanced to install two additional counters. Acetylene is first produced from the sample materials (using lithium carbide) and is subsequently converted to ethane for counting purposes. Dr. Wendt reports that very good plateaus are obtained with C_2H_6 as a counting gas and that he has found it to be much superior to CO_2. To date, he has used the gas satisfactorily up to 4 atmospheres pressure and does not anticipate difficulty in increasing this to 5 atmospheres.

All of the counting equipment is programmed to provide for automatic recording of the output and background information at preselected intervals.

Mineral Separation Laboratory

Procedures followed in the preparation of mica concentrates are essentially the same as those discussed in the description of Dr. Jäger's laboratory in Bern. One additional piece of equipment, an air current sieve, is used to remove all dust from the micas after they have been ground in alcohol. It has been shown that the removal of dust tends to lower the common strontium content determined for the samples.

7. England

Department of Geology and Mineralogy, Oxford University

The isotope laboratories are currently housed in very cramped quarters that have been made more confining as a consequence of construction activity on a new wing of the building. The completion of the addition will, however, provide desperately needed space for the installation of new scientific apparatus.

At present the major emphasis is being placed on studies involving age measurements based on the Rb-Sr and K-Ar ratios, while lead isotope studies and U-Pb, Th-Pb age measurements assume a secondary position.

The staff, under the general direction of Professor L.R. Wager, comprises Drs. S. Moorbath, M. Dobson, E. Hamilton, St. Lambert and Dr. N.J. Snelling who has been seconded to Oxford from the Overseas Geological Survey. In addition to graduate students, two technical assistants are employed on a full time basis. Dr. Snelling is responsible for the supervision of K-Ar age measurements being carried out on behalf of the various Commonwealth Geological Surveys and has the full time assistance of two technicians in this work. During 1962, 75 K-Ar age determinations were completed and in 1960 and 1961 a total of 63 were processed. His project has benefited greatly from the invaluable contribution of Dr. Dobson who designed and assembled the mass spectrometric apparatus used for argon analyses. Other members of the group appear to function quite independently, with each scientist carrying out chemical extractions and mass spectrometric analyses of his own sample materials.

Mass Spectrometric Apparatus

An M.S. 5 (Associated Electrical Industries) solid source mass spectrometer is used for all Rb, Sr and Pb isotopic analyses. The unit embodies a triple filament source assembly mounted in a vacuum lock which permits rapid sample change. A conventional electron multiplier is employed for ion current amplification. Considerable difficulty was being experienced as a consequence of poor peak shape and a lack of concordance between the ion currents recorded when scanning up or down the mass range. This apparently is a function of the relative position of the analyzer tube and magnet. Adjustment of the tube position in the magnet gap is not conveniently realized with this mechanical arrangement and consequently the difficulty is not readily overcome.

The vacuum lock assembly functions very well and permits the rapid introduction of new samples. However, it suffers from the fact that the complete assembly must be dismantled to facilitate removal of the source plates for cleaning. Since this is a very time consuming operation it is not carried out more frequently than is absolutely necessary. Particular care must therefore be taken to ensure that the analyses are not in error as a consequence of contamination arising from preceding samples.

A gas source mass spectrometer embodying a Reynolds type glass analyzer tube has been assembled and is used exclusively for argon analyses. Provision has been made for the easy removal of the magnet assembly to permit the lowering of a bakeout oven over the analyzer tube. Gas samples are admitted to the source region via a Granville-Phillips variable molecular leak, the ion current intensity being adjusted to the desired level by regulating the flow of the gas from the extraction apparatus. This instrument has a very high sensitivity partially realized as a consequence of the slow pumping speed of the vacuum system, and additional sensitivity may be realized by operating the apparatus statically. Under these operating conditions however, one observes a continually varying ion current intensity which must be corrected back to zero time in order to obtain the correct isotope abundance data. The unit is not equipped with an electron multiplier.

The analyzer tube, being fabricated of glass, has been coated on the inside surfaces with a conducting layer of stannous oxide. Hydrochloric acid was used in the application of this coating and consequently a very troublesome residual ion current is observed at mass 36. This, of course, makes it difficult to accurately measure the Ar^{36} isotopic abundance, on which all atmospheric argon corrections are based, and great care must be taken to prevent this residual from increasing. Apparently the introduction of samples containing traces of methane tend to produce an enhancement of the mass 36 residual ion current thereby compounding the problem.

A third mass spectrometer (Associated Electrical Industries M.S. 10), designed for residual gas analysis, has been purchased and is currently used to provide rapid analyses of gases released from various minerals under conditions of controlled temperature. This is a very compact type of mass spectrometer, having a mass resolution of about one part in 40, and is ideally suited to problems requiring the rapid semiquantitative assay of gases in the low mass range. It has not been designed, however to provide the precise abundance determinations essential for K-Ar age measurements.

Delivery of a new Associated Electrical Industries M.S. 2 mass spectrometer is expected to coincide with the completion of construction of the new laboratory quarters. This mass spectrometer is to be used exclusively in the Rb-Sr age determination program.

Argon Extraction Apparatus

The extraction procedures used are essentially the same as those employed in our laboratory with the following minor variations. A stream of air is used to control the temperature of the vacuum fusion chamber in lieu of the water jacket customarily employed. The rare gas is purified over titanium sponge mounted within the fusion chamber and brought up to temperature with the same induction coils used to fuse the sample. A calibrated volume is used to apportion the argon-38 spike to be mixed with the sample gas. This method is considerably more rapid than the conventional system of individually calibrated volumes. However, in this instance, the calibrated volume is defined by two glass stopcocks and the enriched gas is permitted to come into contact with the stopcock grease. The simple arrangement observed in the Max Planck Institute in Heidelberg was designed to overcome this disadvantage. Finally, the extracted argon was permitted to flow through a long glass tube extending across the laboratory (a distance of about 10 feet) directly to the mass spectrometer which is permanently connected to the extraction apparatus. The isotopic analysis is completed immediately and the remaining gas is exhausted to the atmosphere. While it is indeed convenient to have a mass spectrometer permanently attached to the extraction line, much time may be lost if the instrument is not in operating condition when an extraction is scheduled. This problem could, however, be overcome by providing a means of storing sample materials for future isotopic analysis.

Chemical Preparation Laboratory

During the construction period, the space available for chemical processing of sample materials has been considerably reduced. Consequently, the one laboratory now used is terribly crowded. In addition, as pointed out previously, many scientists use the facilities to prepare their own materials and consequently each man appears to function in his own little corner. It is hard to imagine that the common Sr and Pb blanks can be held to a satisfactorily low level when operating under these conditions.

Chemical techniques employed are essentially identical to those developed by Dr. E. Jäger. Quantities of reagents are kept to a minimum in order to reduce the possible introduction of contaminants. Some of the scientists measure their Rb and Sr spike concentrations by volume while others determine the quantity by weight. Dr. Hamilton reports successful Sr purification using columns containing zirconium phosphate. The columns used are much smaller (3-7" long) than those customarily employed. However, the preliminary chemical treatment appears to be much more exacting than the procedures normally followed when Rb and Sr separations are required.

Atomic Energy Research Establishment, Harwell

A very brief visit to one of the mass spectrometer laboratories at Harwell was arranged by Dr. Snelling who very kindly drove me from Oxford to Harwell.

Several types of mass spectrometers were observed under development or in operation. Of these, the most interesting from my point of view, was an M.S. 5 unit which was being modified to permit the simultaneous introduction of six solid samples to the source region. A mechanical arrangement has been developed to facilitate the movement of individual samples to the analyzer region without disruption of the vacuum. This system not only permits the rapid comparison of a number of samples but allows one to re-analyze samples to check on instrumental variations etc. This technique, when perfected, should permit the precise determination of very small isotopic differences between solid samples.

A new solid source current supply has been developed to operate in conjunction with this apparatus. The unit is designed to provide a much more stable current to the filament thereby reducing fluctuations in the number of ions produced at the surface of the sample filament.

Department of Geodesy and Geophysics, Cambridge University

The mass spectrometer laboratory, associated with the Department of Geodesy and Geophysics of the University and under the direction of Dr. J.A. Miller, occupies an isolated one story laboratory building. The group is concerned only with K-Ar age determination techniques and all aspects of the work, including mineral separations, chemical determinations, gas extraction and mass spectrometry are carried on in the single laboratory.

The services of a well equipped machine shop, located nearby, are available to the group. The permanent staff of four technicians is augmented by graduate students and visiting scientists.

Argon Extraction Apparatus

Every effort has been made to reduce the volume of the extraction apparatus which has been fabricated for the most part from stainless steel. Only the small tubes containing charcoal and the vacuum fusion chamber have been made of pyrex glass. A high frequency generator is employed to fuse the samples in the conventional manner. All high vacuum valves, embodying copper seals on stainless steel knife edges, and stainless steel diaphragms, have been designed and fabricated in the laboratory machine shop. One outstanding feature of the valves is the ease with which the stainless steel diaphragm may be replaced in the event of failure. A variation of the valve design comprising two units fabricated back-to-back, and defining a precisely calibrated volume between the copper seals, is used to apportion the argon-38 spike mixed with the radiogenic argon released from the minerals. Plans are now being made to incorporate a modified version of this type of valve into the G.S.C. argon extraction apparatus.

The water jacket used to conduct the cooling water around the fusion vessel comprises a very simple arrangement consisting of a cheap outer glass envelope having the form of a large bore test tube. This is placed over the reaction chamber and the water seal between the two vessels is made by placing a rubber 'O' ring between the base and the outer vessel.

The procedure followed in cleaning up the gases released when the sample is fused varies somewhat from the conventional method. All of the gas released is first cleaned up over hot titanium sponge, the argon-38 spike is then mixed with the residual gas and this combination is again exposed to the titanium sponge before being admitted to the mass spectrometer. Copper oxide is not used.

The extraction apparatus is permanently attached to the mass spectrometer and all samples are analyzed immediately after extraction.

Mass Spectrometric Apparatus

The instrument currently being used for argon analysis is a rather old unit of home manufacture. Dr. Miller apparently inherited many of the components when he arrived at Cambridge and it is to his credit that he has been successful in placing the equipment on an operational footing. The analyzer tube is made of stainless steel and has a 4.5 inch radius of curvature.

One very interesting feature of the arrangement concerns the method of sample introduction. The argon samples are conducted through a metal high vacuum valve, designed as noted above, but with a special copper insert in the central opening. A very fine hole has been drilled in the insert to serve as a molecular leak for the gas. When the valve is closed the analyzer tube is completely isolated from the extraction line, but when it is open the gas sample is permitted to flow through the small leak to the ion source of the mass spectrometer. This design has the added advantage that the size of the leak bore may be easily altered to suit the problem at hand.

The mass spectrometer is equipped with a Vibron type vibrating reed amplifier which appears to function well. An electron multiplier is not used.

Dr. Miller is now assembling the component parts of an Omegatron which he hopes will prove to be more sensitive than the mass spectrometer currently in use. The Omegatron unit, marketed by Philips Industries in Holland, is to be mounted in the pole gap of a very large water cooled magnet having a field strength of 18,000 gauss. The magnet current is to be supplied from a Raydyne motor generator set designed to provide 30 amperes output continuously. A commercial r.f. high voltage supply has been purchased as has a complete Balzers vacuum system embodying oil diffusion pumps and zeolite absorbent traps to prevent the passage of oil vapours from the pumps into the Omegatron chamber. The apparatus on hand is very large and takes up much more room than a conventional mass spectrometer. A great deal of work is required before the preliminary tests may be carried out.

K-Ar Age Determinations

No attempt will be made to summarize all the work being carried on but two items warrant particular mention.

A project to test the suitability of basaltic rocks for K-Ar age measurements has been undertaken. Whole rock samples selected from a drill core from the Whin Sill, situated in Northern England, were used for this study. Ages ranging from 130 m.y. to 305 m.y. were determined for seven samples from the sill. It was noted that the degree of argon retention was not related to the size of the feldspar laths but rather to the degree of alteration of the ground mass, the most altered samples yielding the younger age. It has long been known that feldspars tend to lose a portion of their radiogenic argon, however this may not be a serious problem for samples taken from depth if the argon has been retained within the rock as a whole. To test the hypothesis that argon released from the feldspars may be retained along the grain boundaries of the fine-grained groundmass a sample of dolerite (from the 771' level) was ground and the age determined for the powder was compared with that found for the whole rock. It was observed that the grinding process had liberated 7½% of the argon and that the age of the powder was 260 m.y. compared with 280 m.y. determined for the whole rock. This sample had a relatively unaltered matrix and only the argon occupying sites along the grain boundaries was released on grinding.

The age of intrusion of the sill has been estimated by taking the average of the results of five measurements on the least altered samples. This yields an age of 281 m.y., or Upper-Carboniferous, in keeping with geological evidence.

Studies designed to establish the temperature of liberation of radiogenic argon from minerals and rocks are also underway. A small thermocouple has been designed which may be placed at the surface of the sample melt in order to precisely determine the temperature of the melt when the gas is released. Each fraction of gas is collected and mixed with enriched argon-38 and the quantity is then determined mass spectrometrically.

Radiocarbon Dating Laboratory, Cambridge University

Current studies are primarily concerned with the measurement of the C-14 activity in samples of gas collected in the troposphere. Aircraft flying at altitudes of 40,000 to 46,000 feet have been equipped with special wing pods filled with zeolite. The pods are opened at the desired altitude and the gases are adsorbed in the previously outgassed zeolite. As much as 10 litres of CO_2 may be obtained in a single sample. The C-14 activity, which is several orders of magnitude greater than that found at the earth's surface, is then determined in a conventional proportional counter.

The counter employed for this work has an active volume of 1.5 litres and a background count of 10 c/m at two atmospheres pressure. It is made of a quartz tube that has been mounted in a copper shield.

A very neat gas sample storage system has been set up. With this arrangement it is possible to select gas for measurement from any one of several dozen large storage vessels. A colour-coded schedule of all sample operations is maintained on the laboratory wall, thereby providing up to the minute information re sample processing.

An associated Electrical Industries M.S. 3 mass spectrometer had been purchased and was being modified to permit rapid simultaneous collection analysis of CO_2 samples. This instrument was fitted with a low pressure inlet system similar to the arrangement observed in the Göttingen laboratories. However, I was informed that it did not suffer from the long time lag between samples noted for the Atlas mass spectrometer.

A new method for CO_2 sample preparation, comprising a high pressure bomb, was being tested. The sample, mixed with magnesium perchlorate, is placed in a brass cylinder, 4" O.D. x 6" long, having an 'O' ring seal at the cover. A coil has been mounted on a conventional spark plug which is mounted in the cover. The sample is fired by applying a high voltage to the coil which is positioned in the sample within the vessel. In this manner a two gram sample of peat may be converted to CO_2 instantaneously.

Associated Electrical Industries Ltd., Trafford Park, Manchester

A very enjoyable day was spent in the company of Drs. John Waldron and John Halliday at the mass spectrometry assembly plant in Manchester. Permission to visit the group and all arrangements for the trip were very kindly made by Mr. Derek Kingsbury, assistant to the Chairman of the Board of A.E.I., 33 Grosvenor Place, London.

The following types of mass spectrometer were observed under construction and/or being tested. Brief accounts only will be included here, detailed information is on file in the Isotope Geology Section.

M.S. 2 - A six inch radius, gas source mass spectrometer, fitted with an automatic sensitivity selector and used extensively in industry. This model is also sold with a vacuum lock for use with a solid sample source. (See account of laboratory at Clermont-Ferrand, France). The University of Toronto has an early model of this type.

M.S. 3 - A smaller unit (4½" radius) now being converted for simultaneous collection of gas samples. (See report of Cambridge Radiocarbon Laboratory).

M.S. 5 - A 12" radius solid source instrument fitted with a very good vacuum lock and electron multiplier ion detection system. This is the best high mass solid source mass spectrometer on the market and it is ideally suited to the analysis of lead, uranium, thorium and plutonium. (See account of visit to French Atomic Energy Laboratories, Saclay, France).

M.S. 7 - A spark source double focusing mass spectrometer of the Mattauch type, having a resolving power of one mass unit in 2500, and embodying a photographic plate detector to record ion intensities. A novel probe has been designed to ascertain the charge arriving at the photographic plate. This information is fed-back to regulate the spark source and to time the exposure of the plate. This equipment may be used to analyze all elements and is particularly useful for the detection of trace impurities of elements in quantities as small as 1 part in 10^9 of the major constituent of the sample. It may be employed for either quantitative or qualitative analysis of inorganic solids. Most elements are readily detectable to 0.01 ppm or better.

M.S. 9 - This instrument comprises two 90° deflection units, one an electrostatic analyzer, the other a magnetic analyzer, mounted in tandem. It has a guaranteed resolution of 1 mass unit in 25,000. The mass spectrometer is designed for the precise determination of atomic mass differences, and provision is made for one to read the mass difference between two ions to six decimal places, directly from the control dials of the instrument. It is primarily designed for the analysis of heavy hydrocarbons but a solid source is now being designed.

M.S. 10 - A one piece, 2" radius, residual gas analyzer with a resolution of 1 mass unit in 40. The unit is designed for vacuum monitoring, leak detection, analysis of gases in metals, monitoring chemical reactions, etc. The equipment has not been designed for the precise isotopic abundance measurements.

Microprobe - A very compact instrument with vacuum spectrometer mounted on top. Designed for 0.3 micron beam. The unit appeared to be quite versatile.

REFLECTIONS

In all of the laboratories visited plans are being made to expand the age determination facilities to embrace more than one method of geological age measurement. It is noteworthy that Rb-Sr techniques have been employed by the majority of European laboratories for some time, and that the apparatus required for K-Ar studies is now being acquired. This line of development, which is the opposite to that followed in the majority of North American institutions, probably reflects the period of disenchantment with K-Ar results coincident with the time when European laboratories were being established. However, it has become increasingly evident that geological processes affect the elemental ratios in diverse ways, and that a knowledge of more than one parent-daughter ratio is essential to the satisfactory interpretation of the results obtained, especially when studying complex geological regions. The two methods currently in use provide the maximum contrast available in this regard, since one is based on the accumulation of a volume of gas and the other on the incrementof an isotope in the solid state. Most groups are also anxious to extend their capabilities to include the determination of the U-Pb and Th-Pb ratios found in zircons and other uranium bearing minerals.

Mass spectrometers are now being marketed by European firms and many of these units have been purchased for isotope laboratories in spite of the fact that extensive modifications are often required to adapt the units for application to geological problems. This did not prove to be a major obstacle for those groups comprising scientists specializing in physics and chemistry as well as geology. It was, however, noted that in some instances the mass spectrometers were not functioning properly and that none of the laboratory staff appeared to be aware of the trouble.

Questions were often asked regarding the activities of other laboratories that I had visited. It was indeed surprising to me to note the apparent lack of knowledge of the work of laboratories located within a few hundred miles of one another. It would appear that nationalism dies hard!

The personal contacts have already proven to be of value to our work and I am sure we shall continue to reap the benefits of this association. I was received in a most hospitable manner and I found everyone anxious to learn of the activities of the Geological Survey of Canada.

APPENDIX 1

Laboratories visited in chronological order

Laborary	Address	Date	Scientists Contacted
Laboratory for Mass Separation	407 Kruislaan, Amsterdam, The Netherlands.	April 22-23	Dr. J. Kistemaker Dr. A.E. de Vries Dr. T. van Der Hauw
Laboratory for Isotopen-Geologie	407 Kruislaan, Amsterdam, The Netherlands.	April 22-23	Dr. H.N.A. Priem Dr. N.A.I.M. Boelrijk Dr. A.J.H. Boerboom
University of Amsterdam	Nieuwe Prinsengracht 130, Amsterdam, The Netherlands.	April 23	Prof. W.P. De Roever Dr. H.N.A. Priem
Institut de Physique	Université Libre de Bruxelles, Avenue F.D. Roosevelt 50, Bruxelles 5, Belgium.	April 24	Prof. E. Picciotto Dr. R. Delwiche Dr. S. Deutsch
Musee Royal de L'Afrique Cêntrale	Tervuren, Belgium.	April 25	Dr. L. Cahen
Centre de Physique Nucléaire	Université de Louvain, Parc D'Arenberg, Hévérle, Belgium.	April 25	Dr. E. Crèvecoeur
Centre D'Études Nucléaires de Saclay	Boite Postale No. 2, Gif-sur-Yvette, Siene-et-Oise, France	April 26	Dr. E. Roth Dr. G. Dirian Dr. M. Dupuis Dr. Labeyrie Dr. Botter
École Nationale Supérieure de Geologie Appliquée et de Prospection Minère.	Université de Nancy, 94 Avenue de Lattre de Tassigny, Boite Postale, No. 452, Nancy, France.	April 30	Dr. G. Durand Dr. R. Coppens Mr. Kostolanyl Mr. Govindaradju Mr. Jurain Mr. Richard Mr. Sonnet Mr. Kaplans
Laboratoire de Géologie et Minéralogie	Université de Clermont, 3, rue Louis Kessler, Clermont-Ferrand, France	May 2	Prof. M. Roques Mr. Y. Vialette Mr. M. Bonhomme Dr. Fransisco Mendes (Lisbonne, Portugal).

Laboratory	Address	Date	Scientists Contacted
Laboratorio di Geologia Nucleare	Universita Pisa, Via S. Maria 22, Pisa, Italy	May 5-6	Prof. E. Tongiorgi Prof. G. Dessau Dr. G. Ferrara Dr. A. Longinelli Dr. R. Gonfiantini
Mineralogical Institute	Universität Bern, Sahlistrasse 6, Bern, Switzerland.	May 8-9	Dr. E. Jäger Dr. E. Niggli Dr. Th. Hugi
Physikalisches Institut	Universität Bern, Sahlistrasse 6, Bern, Switzerland.	May 8-9	Prof. J. Geiss Prof. H. Oescheger
E.T.H. Mineralogical Institute	Sonneggstrasse 8, Zurich, Switzerland.	May 10	Prof. Marc Grunnenfelder
Max-Planck-Institut fur Kernphysik	Jahnstrasse 29, 69 Heidelberg, Germany	May 13	Dr. J. Zähringer Dr. H.J. Lippolt
Physikalisches Institut der Universität Heidelberg	Philosophenweg 12, Heidelberg, Germany.	May 13	Dr. K.O. Munnich
Zentrallaboratorium für die Geochemie der Isotope	Universität Göttingen, Lotzestrasse 16/18, Göttingen, Germany.	May 15	Prof. C.W. Correns Dr. H. Nielsen Dr. Schnieder Dr. H.K. Wedepohl
Bundesanstalt für Bodenforschung	Wiessenstrasse 1, Hannover, Germany.	May 16	Dr. Immo Wendt Dr. H. Lenz
Department of Geology and Mineralogy	University Museum, Oxford, England.	May 20-21	Prof. L.R. Wager Dr. N.J. Snelling Dr. M. Dobson Dr. S. Moorbath Dr. E. Hamilton Dr. C. Evans Dr. U. Aswathanarayana
Atomic Energy Research Establishment	Harwell, Berkshire, England.	May 21	Dr. R.K. Webster Dr. A.H. Turnbull
Dept. of Geodesy and Geophysics, Cambridge University	Madingley Rise, Madingley Road, Cambridge, England.	May 22	Prof. Sir E. Bullard Dr. J.A. Miller
Radiocarbon Dating Laboratory	Cambridge University, 5 Salisbury Villas, Station Road, Cambridge, England.	May 22	Dr. E.H. Willis

Laboratory	Address	Date	Scientists Contacted
Associated Electrical Industries Limited	Trafford Park, Manchester, England.	May 24	Dr. J. Waldron Dr. John Halliday
Associated Electrical Industries Limited	33 Grosvenor Place, London S.W. 1, England.	May 25	Mr. Derek Kingsbury

APPENDIX 2

European Hotels

Name	Address
Southway Hotel	Gillingham Street, London, S.W. 1, England.
Hotel Banen	5 de Lairessestraat, Amsterdam, The Netherlands.
Hotel Albergo	58, Ave. de la Toison d'Or, Brussels, Belgium.
Hotel Scribe	1 rue Scribe, Paris, France.
Hotel Thiers	Nancy, France
Grand Hotel	44 Av. des Etats-Unis, Clermont-Ferrand, France.
Grant Hotel "Duomo"	Pisa, Italy
Hotel Regina	Bern, Switzerland
Hotel Leoneck	Leonhardstrasse 1, Zurich, Switzerland.
Hotel Colombi	Freiburg, Germany
Hotel Europaischer Hof	Heidelberg, Germany
Gebhards Hotel	Goetheallee 22-23, Göttingen, Germany.
Hotel Kronprinz	Göttingen, Germany.
Randolph Hotel	Oxford, England.
Midland Hotel	Manchester, England.

APPENDIX 3

European Manufacturers

Items	Address
Wilfley type table for concentration of minerals $600.00	Wedag, Westfallia, Dinnendahl, Groppell, A.G. Bochum, near Dortmund, Germany.
Poly-vinyl-chloride fume hoods. Trade name 'Covidur'	Lacollonge-Flexone S.A. Villeurbanne-Lyon, France. OR P. Lacollonge-Belgique, 56 rue des Aciens Combattants, Zunn-Les-Bruxelles, Belgium.
Geiger tubes - for C-14 guard ring.	Laboratoirie Centrale, Telecommunications, 46 Av. d Breteruil, Paris VII, France.
Small metal bellows for metal vacuum systems	Socomec, 513 Rue Gabriel Peri, Colombes (Seine) France.
Platinum - 1500° C. furnace	Adamel, 4-5 Passage Louis Phillipe, Paris XI, France.
Paramagnetic analyzer (Forrer) $1000.00	Electrona, Lingolsheim, Bas-Rhin, France.
Quartz water still 0.4 l/hr.	Heraeus, Hanau am Main, Germany.
Magnetic separator	Saima - M, Via del Politecmico 3, Milano, Italy.
Electron multiplier assemblies - $100.00	Valvo GMBH, Hamburg 1, Germany.

Items	Address
Resistors	Pyrofilm Resistor Co., U/S Highway 46, Parsippany, New Jersey, U.S.A.
Air Current Sieve, Alpine	Luffstrahl-Siev, Augsburg P.O. Box 629, Germany.
Large bore vacuum valves and mercury diffusion pumps	Leybold Ltd.,
Electron Multiplier Assembly - 17 stage. Cu-Be dynodes.	E.H.T. Zurich, Switzerland.
Mass Spectrometers	
Atlas	Atlaswerke, Bremen, Germany
Houston-Thompson	Houston-Thompson Co., Paris, France.
A.E.I.	Associated Electric Industries, Trafford Park, Manchester 17, England.

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